

Charged State of Freshly Nucleated Particles: Implications for Nucleation Mechanisms

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Abstract Aerosol nucleation events have been observed at a variety of locations worldwide, and may have significant climatic and health implications. Despite extensive studies in the past, the mechanisms of particle formation remain illusive. While ions have long been suggested as favorable nucleation embryos, their significance as a source of atmospheric particles has remained uncertain. An analysis of recent measurements of the electrical charge on freshly nucleated particles can shed new light on the underlying nucleation mechanisms. Here, we demonstrate, based on a conservative analytical analysis and detailed kinetic simulations, that ion-mediated nucleation (IMN) can consistently explain the charged states of new particles, and particularly the excess charge (or overcharging) most frequently detected. We contrast our results to other analyses of these measurements, which conclude that the ion contribution to particle formation is relatively small, and demonstrate that the ion contribution may in fact be dominant.

Keywords Nucleation theory, ion-mediated nucleation, electrical charge state, charged fraction

Mechanisms of Atmospheric Particle Formation

Measurements indicate that H_2SO_4 and H_2O are clearly involved in many, if not most, nucleation events observed in the atmosphere. Binary homogeneous nucleation of sulfuric acid and water is now generally taken to be negligible in the lower troposphere.¹ Recent analyses of laboratory measurements also show that the contribution of ternary homogeneous nucleation, which involves ammonia, to the formation of new particles is likely to be very limited.² While certain organics have been shown to enhance H_2SO_4 - H_2O nucleation rates in the laboratory,³ the level of

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enhancement is similar to that of ammonia, and the significance of organics in initiating nucleation is probably small. On the other hand, organics clearly contribute to the growth of freshly nucleated particles.

Ions, which are generated continuously and ubiquitously throughout the atmosphere by cosmic radiation and radioactive decay, have long been known to promote nucleation. To study nucleation processes involving ion clusters, Yu and Turco^{4,5} developed a kinetic model that explicitly treats the complex interactions among small air ions, neutral and charged clusters of various sizes, precursor vapor molecules, and the preexisting aerosol. Yu and Turco⁵ refer to the coupled formation and evolution of aerosol size distributions, including both charged and neutral clusters – under the influence of ionization, recombination, neutralization, condensation, evaporation, coagulation, and scavenging – as ion-mediated nucleation (IMN). This IMN model has been updated by incorporating recently available thermodynamic data and algorithms.⁶

The multiple-year ion charge and mobility measurements taken in Hyttälä, Finland indicate that ions are involved in more than 90% of the particle formation events that can be clearly identified.^{7,8} Nevertheless, the relative importance of IMN versus neutral nucleation in the atmosphere remains unclear. Laakso et al.⁷ conclude that the average contribution of ion nucleation to the overall nucleation rate is relatively small. Yu⁹ points out, however, that the same measurements presented by Laakso et al.⁷ may actually indicate the dominance of IMN in the observed particle formation. Accordingly, a careful interpretation of the measured charged fractions of freshly nucleated particles is needed to identify the underlying nucleation processes.

Overcharging of Freshly Nucleated Particles

We assume that IMN, and classical homogeneous (neutral) nucleation, create thermodynamically stable particles at rates, J^{IMN} and J^{HOM} , respectively, with an initial diameter, $d = d_0$. It should be noted that the formation rates of neutral particles will generally be enhanced by IMN through ion–ion neutralization processes involving sub-critical clusters, which is ignored here. Thus, the analysis below is conservative with regard to the contribution of IMN to the overall nucleation rate. Under these assumptions, the fraction of new particles that are initially charged (i.e., the charge fraction, CF) would be approximated as,

$$\text{CF}(d_0) = J^{\text{IMN}} / (J^{\text{IMN}} + J^{\text{HOM}}) \quad (1)$$

This fraction applies only to particles nucleated during a specific time interval that is short relative to variations in the nucleation rates. Generally, these particles will grow into larger stable aerosols within a definite size range.

The particles nucleated on ions are quickly neutralized due to recombination during their initial growth. Thus, as the particles increase in size from d_0 to d_1 ,

the fraction originally nucleated on ions (i.e., at a rate, J^{IMN}) that remain charged at $d = d_1$ is roughly,

$$X^C = e^{-\alpha C \Delta t} \quad (2)$$

where α is the ion-ion recombination coefficient for a small ion with a charged nanoparticle of opposite sign, and C is total concentration of small (negative or positive) ions. Here, $\Delta t = (d_1 - d_0)/GR$ is the time needed to grow particles from d_0 to d_1 at a fixed growth rate, GR .

An aerosol immersed in a steady-state ion-plasma achieves an *equilibrium* (or steady-state) charge distribution. Hence, the attachment of small ions to neutral particles also contributes to the charged fraction, and we identify $CF'(d_1)$ as the charged fraction at $d=d_1$ due to this contribution. $CF'(d_1)$ is always smaller than the corresponding equilibrium charged fraction $CF^0(d_1)$, because charging of a neutral aerosol approaches equilibrium from lower charge values. Under transient conditions, the ratio of an instantaneous CF to the equilibrium CF^0 at the same size is defined as the overcharge ratio, OR . The values of OR for particles at $d = d_1$ can be estimated as follows,

$$OR \leq [CF' \times (J^{\text{IMN}} + J^{\text{HOM}}) + X^C J^{\text{IMN}}] / [CF^0 (J^{\text{IMN}} + J^{\text{HOM}})] < 1 + e^{-\alpha C \Delta t} \times J^{\text{IMN}} / [CF^0 \times (J^{\text{IMN}} + J^{\text{HOM}})] \quad (3)$$

The particles are overcharged if $OR > 1$, and undercharged if $OR < 1$. Under typical conditions, $\alpha = \sim 1.5 \times 10^{-6} \text{ cm}^3/\text{s}$, $C = \sim 750/\text{cm}^3$. The growth rates of sub-3 nm intermediate ions at Hyytiälä have been estimated from ion mobility spectra to be in the range of $\sim 0\text{--}4 \text{ nm}/\text{hour}$ with a mean value of $1 \text{ nm}/\text{hr}$.¹⁰ If we assume $d_1 = 3 \text{ nm}$, $d_0 = 1.5 \text{ nm}$, and $GR = 1.5 \text{ nm}/\text{hr}$ (for sub-3 nm particles), we determine,

$$OR(3 \text{ nm}) < 1 + 0.017 J^{\text{IMN}} / [CF^0 (J^{\text{IMN}} + J^{\text{HOM}})] \quad (4)$$

The equilibrium charged fraction $CF^0(d)$ at $d = 3 \text{ nm}$ is around 1%. From equation (4) we can then estimate OR for particles of 3 nm for several scenarios:

Case 1: 100% IMN nucleation, $J^{\text{IMN}}/(J^{\text{IMN}} + J^{\text{HOM}}) = 1.0$: $OR < 2.7$

Case 2: 50% IMN nucleation, 50% homogeneous nucleation: $OR < 1.85$

Case 3: 10% IMN nucleation, 90% homogeneous nucleation: $OR < 1.17$

Case 4: 100% homogeneous nucleation: $OR < 1$

For the 27 nucleation event-days described by Laakso et al. (2006), in which $OR(3 \text{ nm})$ values are given, the following data apply: $OR(3 \text{ nm}) > 2$ for 20 days (74%); $1 < OR(3 \text{ nm}) < 2$ for 5 days (18.5%); and $OR(3 \text{ nm}) < 1$ for 2 days (7.5%). Thus, based on a simple, and conservative, interpretation, these measurements⁷ indicate that IMN dominates particle formation on most of the days sampled. Of course, the analysis is subject to uncertainties associated with the values of α , C and GR . In real situations, α and GR depend on the size and type of particles, and α , C and GR also vary with time during nucleation events. Accordingly, full kinetic modeling with resolved microphysics is required to resolve the effects of such variations.

We simulated this competitive, highly nonlinear homogeneous/ion nucleation regime using a model that explicitly resolves positive, negative, and neutral particles ranging in size from molecular scales to several micrometers, while also treating the co-condensation of sulfuric acid and organic compounds.⁶ Figure 1 provides a comparison of simulated and observed size-dependent OR values. The predicted rapid decrease in OR as particle sizes increase from ~ 2 –3 nm to 7 nm is consistent with measurements. It appears that most of the observed behavior in OR can be explained in a straightforward way by variations in the concentrations of the key precursor gases (sulfuric acid and low volatility organics), and by sensitivity to the particle size at which organic vapors begin to condense (the activation size).

An overcharge on freshly nucleated particles is an unambiguous signature of an IMN mechanism. Based on our simulations, competing neutral H_2SO_4 - H_2O and ternary nucleation are negligible under the conditions encountered. Thus, practically all of the neutral particles between 1–3 nm are formed via the neutralization of charged particles, while activation and growth of these 1–3 nm particles provides the major source (>90%) of the aerosol detected at sizes ≥ 3 nm. Laakso et al.⁷ interpreted the

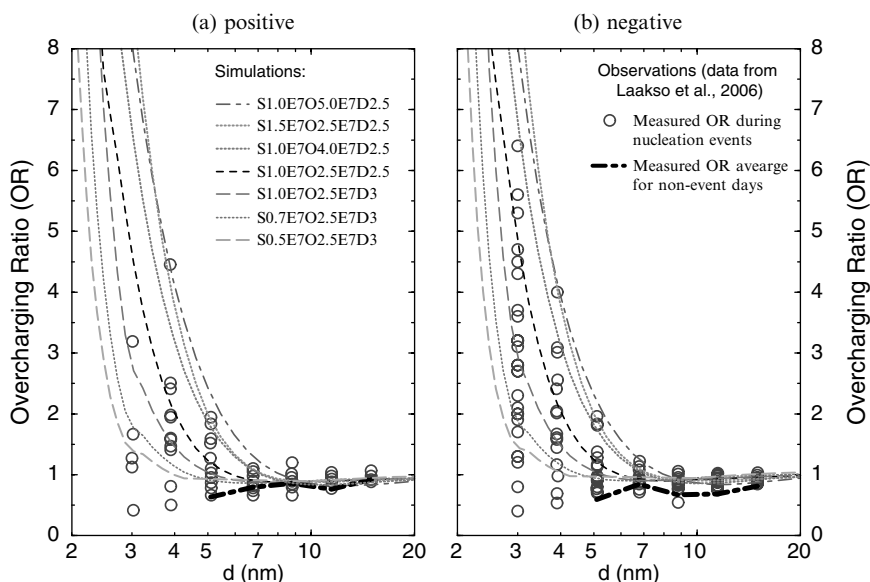


Figure 1 Simulated and observed size-dependent overcharging ratios (ORs) are compared. Each curve represents calculated OR values averaged over nucleation events corresponding to specific atmospheric conditions (**below**). The open circles are observed OR values for 34 nucleation events sampled with an ion-DMPS during an intensive field campaign reported by Laakso et al.⁷; the thick dashed lines are mean ORs seen on 5 nonevent days. In the simulations, temperature (T), relative humidity (RH), and precursor gas concentrations (sulfuric acid [S], condensable organics [O]) were parameterized as sine functions of local time to mimic diurnal variations. In the legend, read S1.0E7O5.0E7D2.5 as $[\text{S}]_{\text{max}} = 1.0 \times 10^7 \text{ cm}^{-3}$, $[\text{O}]_{\text{max}} = 5.0 \times 10^7 \text{ cm}^{-3}$, and $D_{\text{act}} = 2.5 \text{ nm}$ (the particle activation diameter for organic condensation). The daily mean T and RH (i.e., T0 and RH0) are 270 K and 60%, respectively

same overcharge measurements and concluded that the average contribution of IMN to the total nucleation rate is relatively small. Here, both a conservative analytical analysis and a detailed kinetic modeling assessment, confirm that the contribution of ion nucleation is dominant. We suggest that the analysis of particle electrical overcharging data requires a comprehensive analytical interpretation accounting for the range of realistic conditions encountered in the field.

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